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Pulsed Fluorescence Monitor for Measuring Ambient Nitrogen Dioxide Development of a Laboratory Prototype

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A prototype pulsed flashlamp monitor for measuring ambient NO_2 has been developed, constructed and tested. The basic principles are similar to a laser fluorescence NO_2 monitor developed 3 years earlier by the Electronics Research Lab of the Aerospace Corp. The pulsed system has met the contract design goal of a sensitivity of 5 ppb for an integration time of 1 minute, and shows great promise for further improvement. The systems operation has been successfully demonstrated in monitoring outside air. Continued development will lead to an instrument comparable in compactness to present chemiluminescence instruments while being relatively interference free and more reliable.

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PULSED FLUORESCENCE MONITOR FOR MEASURING AMBIENT NITROGEN DIOXIDE
Development of a Laboratory Prototype

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ABSTRACT

A prototype pulsed flashlamp ambient NO_2 monitor has been constructed and tested. The basic principles are similar to a laser fluorescence NO_2 monitor developed some years earlier at the Electronics Research Laboratory of the Aerospace Corporation. The prototype flashlamp unit has fully met the contract design goal of a sensitivity of 5 ppb for an integration time of approximately 1 min. Its operation has been successfully demonstrated in monitoring the outside air. The unit provides a direct digital read-out in real time of the NO_2 concentration in ambient air. The prototype unit shows great promise for further improvement. Its continued development will lead to an instrument comparable in compactness to present chemiluminscence instruments but probably more economical in cost and certainly more reliable in operation. The freedom from interferences makes the present instrument unique. Many new applications will undoubtedly be pursued which utilize the unique characteristics of the pulsed lamp fluorescence monitor.

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LIST OF ABBREVIATIONS AND SYMBOLS

EPA	Environmental Protection Agency
LINFM	Laser Induced NO_2 Fluorescence Monitor
NERC/RTP	National Environmental Research Center, Research Triangle Park, North Carolina
ppb	parts per billion
PMT	photomultiplier tube
PNFM	Pulsed NO_2 Fluorescence Monitor

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SECTION 1

INTRODUCTION

The objective of this program is to demonstrate the feasibility of a pulsed NO_2 fluorescence monitor (PNFM) for ambient air which is compact and of low cost. Excitation of the NO_2 is provided by a small pulsed xenon filled flashlamp and the concentration of NO_2 is determined by measurement of the characteristic NO_2 fluorescence. The physical principles involved are identical to those considered in the development of a laser-induced NO_2 fluorescence monitor.[1]

A program initiated at the Aerospace Corporation in 1970 has led to the development of unique instrumentation for the monitoring of ambient NO_2 concentrations. This instrumentation is based on NO_2 fluorescence induced by specially selected sources. Several versions of laser-induced fluorescence monitor (LINFM) have been developed.[1-5] A prototype instrument which utilizes a He-Cd laser at 442 nm was developed for the U.S. Environmental Protection Agency (EPA) and has been used in both ambient air monitoring and smog chamber experiments. Accumulated experience with this prototype has established the sensitivity (< 1 ppbv) of the technique as well as a lack of interference from compounds such as water vapor, and various nitrogen containing compounds. However, alternate solutions have been sought to reduce the size and cost of the instrumentation. One such alternative using flashlamp induced fluorescence will be described in this paper. Preliminary design and feasibility studies for the flashlamp system were conducted at EPA/RTP; subsequent development was carried out at the Aerospace Corporation.

The current most widely used technique for measuring ambient levels of NO_2 is chemiluminescence.[6] Commercial chemiluminescence systems convert NO_2 to NO before introducing the sample stream into a reaction chamber in which NO and excess ozone are reacted to give gas phase chemiluminescence. However, the conversion process is not specific to NO_2 and other nitrogenous compounds such as peracetyl nitrate (PAN) also yield NO. Winer, et al[7], has documented

the extent to which a number of nitrogen-containing compounds cause a response in a typical commercial monitor. Since the ratio of atmospheric NO_2 to other nitrogen containing compounds, such as PAN, is normally high, the chemiluminescence monitors provide reliable data to determine compliance with national air quality standards. Under conditions of low concentrations of NO_2 to other nitrogenous compounds (which is a common situation in smog chamber studies but is only rarely encountered in the atmosphere) the chemiluminescence analyzers may suffer significant interference.

The development of a flash lamp NO_2 fluorescence monitor (FLNM) is a significant step towards new instrumentation which offers the advantages of the LINFM with respect to freedom of interference, but, in addition, should be economical, reliable and of simple construction. It is anticipated that further development of the FLNM could result in instrumentation more advantageous than present chemiluminescence instruments and could lead to a widespread utilization of FLNM type of NO_2 monitors.

SECTION 2

CONCLUSIONS

The goals of this contract have been successfully demonstrated. A prototype pulsed flashlamp NO_2 fluorescence monitor has been developed and tested. The instrument displayed a linear response and a detectability of 5 ppb of NO_2. The operating principles are similar to those of the laser fluorescence NO_2 monitor developed earlier at Aerospace Corporation, which was shown to be free of interferences, and consequently, the present instrument should not exhibit any undesirable interferences. Admittedly, it is desirable to test the prototype instrument directly to assess its freedom from interferences.

The instrument was demonstrated to perform satisfactorily in monitoring ambient NO_2 in the vicinity of our laboratory. The prototype shows every evidence of stable, reliable and long life operation.

SECTION 3

DESCRIPTION AND CHARACTERISTICS OF THE PULSED FLUORESCENCE NO_2 MONITOR

DESCRIPTION

A photo of the prototype is shown in Figure 1. The NO_2 chamber is located along the back side of the optical table with the xenon flashlamp housing mounted on the right arm of the chamber. The cooled photomultiplier can be seen in the center foreground mounted on the side of the chamber. The electronic packages are situated on top of the table on both sides of the photomultiplier housing.

OPTICAL SUBSYSTEM

The layout of the optical system, depicted in the diagram of Figure 2, shows the excitation xenon flashlamp and the NO_2 chamber with the side mounted photomultiplier tube.

A USSI (United States Scientific Instruments, Inc.) type 3CP-1 xenon flashlamp is used for excitation. This lamp has axial geometry with an arc length of 1 mm and is mounted with the long axis vertical. The maximum average power input to the lamp is rated at 100 watts (100 joules at 1 pulse per second or .01 joules at 10,000 pulses per second). The life expectancy of the lamp under these circumstances is 3×10^7 flashes, where life expectancy is defined as the number of flashes allowed before the light output will drop to 50% of its original value.

The lamp is driven by a discharge of a 10.6 microfarad capacitor charged to 730 volts (2.8J stored energy). With an energy input of about 2.8 joules, a pulse duration of 6.5 us and a pulse repetition rate of 13 pulses per second, the average input power is 37 watts or about 37% of its maximum rating. Under these circumstances the life expectancy of the lamp should be about 10^8 flashes or close to one year in continuous operation. Typical spectral output of the lamp within the region of interest is shown in Figure 4.

The lamp is placed at the focal point of a 5 cm diameter, 2.5 cm focal length lens. Spatial filtering and collimation of the beam was accomplished by the use of two 5 cm focal length lenses placed 10 cm apart with a 4 mm diameter aperture at the midpoint between them. In order to reject off axis light, the first lens (5 cm diameter) has a 3.8 cm diameter mask directly in front of it and the second lens (2.5 cm diameter) had a 2.5 cm diameter mask. This whole assembly was placed 2 cm from the collecting lens. The beam is introduced into the chamber through a Corning glass CS 0-51 filter and a 5 cm path of saturated $CuSO_4$ solution, respectively. The pass band of this filter combination is shown in Fig. 4. The energy delivered to the NO_2 sample using this filter combination was found to be 80uj per pulse for 2.8J input to lamp. The Corning CS 0-51 filter is used to reject UV light below 400nm. Wavelengths shorter than 400 nm produce dissociation of the NO_2 molecules and are very inefficient in exciting fluorescence. The $CuSO_4$ solution filter absorbs light longer than 580 nm. The filter combination is placed 5 cm from the lamp collimator and 33 cm from the center of the chamber. This distance could be shortened to as little as 12 cm before the fluorescence of the quartz window on the solution filter cell will cause an appreciable increase in background signal.

The entrance to the central part of the chamber is sealed with an air-tight quartz window. A 15 cm f.l. lens is used to focus the beam to a diameter of approximately 1 cm at the center of the field of view of the photomultiplier. Immediately following the lens there is a 1.8 cm mask and 6 cm beyond the lens another 1.5 cm aperture which is 6 cm from the center of the field of view of the PMT. These apertures reduce scattered off-axis light and thereby reduce the background fluorescence. The inside of the front arm is blackened to reduce scattered light. The center portion of the chamber is essentially a 5 cm diameter tube, 12.5 cm long with a 2.5 cm long side arm on which the PMT is mounted for viewing the fluorescence. The inside of this tube was blackened to reduce scattered light. A mask with a 1 cm wide by 2.5 cm long rectangular slot is provided through which the fluorescence is viewed by the PMT. A cylindrical front surface aluminized mirror positioned around the back side of this center section to reflect the fluorescence light into the PMT resulted in doubling the signal.

After exiting the center section, the light beam passes into a 25 cm long rear arm which is blackened on the inside and contains three baffles placed 10 cm apart starting from the end of the center section. The first baffle is 3.2 cm in diameter, while the last two are 3.8 cm in diameter. The beam is absorbed on a blackened "wall" at the end of the rear arm. However, in the center of this "wall", there is a small hole through which the detector for the light integrator controller samples the beam energy. The chamber is sealed with a fused silica window oriented 55.6° with respect to the direction of the incident beam (Fig. 2).

All optical elements, apertures and masks, including their sizes and locations, between the flash lamp and the end of the rear arm were chosen with a view toward minimizing the background signal. Individual elements themselves may only have contributed to a small reduction but in combination with the other elements resulted in a substantial reduction in the background.

The side arm of the chamber is sealed with a quartz window. A 5 cm focal length lens (5 cm in diameter) is used to collect and focus the fluorescence onto the surface of the PMT. Situated between the viewing window and the lens is a 2 cm path length of 304 grams per liter solution of $Na_2Cr_2O_7 \cdot 2H_2O$. This solution filter strongly absorbs the scattered light from the flashlamp without producing detectable fluorescence. However, there is a small overlap in the bandpass of the $CuSO_4$ filter in front of the flashlamp and the $Na_2Cr_2O_7 \cdot 2H_2O$ solution which transmits about .05% at 560 nm. To eliminate the band overlap a Corning CS 2-62 filter with a cutoff at 590 nm was placed in back of the $Na_2Cr_2O_7$ solution filter. The location of this Corning filter is important. If placed in front of the solution filter, the Corning filter would be exposed to the scattered flashlamp light and the resulting fluorescence would again increase the background.

The resultant fluorescence bandpass of the combination $Na_2Cr_2O_7$ solution filter and CS 2-62 Corning filter is shown in Fig. 5.

The detector used for observing the fluorescence is a EMI 9659 QAM photomultiplier with an extended S-20 response, installed in a Products for Research type TE 12 OTS-RF thermoelectric cooled housing with a PFR type 271TSA-9558 dynode chain assembly. The PMT was cooled to approximately -12°C.

Tests on uncooled 9659 QAM PMT indicated a detectability of 11 $\pm$ 3 ppb of NO_2. At this point, it was noticed that the fluctuations of the background signal (which is the limiting factor for our detectability) were of the same order of magnitude as the fluctuations of the PMT dark current signal. Consequently, improved sensitivity could be obtained by cooling the PMT.

On cooling the PMT, the dark current fluctuations were reduced by a factor of 8. The fluctuations in the background signal were only reduced by a factor of 2 and this is in part due to the reduction in the PMT dark current. This reduction in the magnitude of the background fluctuation combined with a 10% increase in sensitivity of the PMT due to cooling, resulted in the present level of detectability, 5.6 ppb $\pm$ 1 ppb.

ELECTRONICS SUBSYSTEM

A block diagram of the electronics system of the laboratory model pulsed NO_2 fluorescence monitor (PNFM) is shown in Fig. 3. The overall operational scheme of the PNFM is that fluorescence photons are generated when light from a pulsed xenon flashlamp excites NO_2 molecules in air drawn through the monitor's examination chamber. A photomultiplier tube senses the fluorescence. Electronic circuitry processes the electrical signal generated by the PMT to provide the NO_2 concentration measurement data. A more detailed operational discussion follows.

During a measurement cycle the flashlamp is controlled either by a flash counter or by an optical energy meter. In the flash counter control mode a specific, selectable number of lamp flashes will occur during a measurement cycle. In the energy meter control mode a fixed amount of optical energy passing through the air examination chamber sets the duration of a measurement cycle. Both lamp control modes were used during the testing phase of the PNFM. For test purposes the number of lamp flashes during one measurement cycle was arbitrarily set to exactly 1000 flashes for the flash counter mode and the optical energy meter controller was set to stop a measurement cycle when an accumulated energy measurement corresponding to about 1000 of these flashes or 80 mJ had passed through the air examination chamber.

Although our test results indicate that both lamp control modes provide almost identical NO_2 detecting capability, the optical energy controller

could be used to compensate for lamp variations, i.e., if a flashlamp's energy per flash were to degrade with time, the optical energy controller would assure that a sufficient number of lamp flashes were added per measurement cycle to produce the pre-selected optical energy. Conversely, if the lamp or its operating conditions were to change such that more energy per flash was emitted, the controller would reduce the number of flashes per measurement cycle to attain the pre-selected energy.

The electronic charge signal (output of the PMT) is processed by the PNFM's electronic circuitry to provide the NO_2 measurement data. The operation of the circuitry is as follows. A capacitor connected to the output of the photomultiplier tube receives the electronic charge when enabled to do so by an electronic switch connected to the terminals of the capacitor. The switch maintains a short circuit across the capacitor terminals at times other than a fixed period that includes the flashlamp operating time. The switch opens for a period of 100 microseconds during which time the lamp flash starts and ends. Since the fluorescence lifetime of the NO_2 molecule is only about 10^{-9} seconds, the photomultiplier responds to the total fluorescence signal by producing an electronic charge on the capacitor that is proportional to the fluorescence signal. The resulting capacitor voltage is buffered by a unity gain operational amplifier stage and presented to another unity gain operational amplifier operating in a sample and hold circuit configuration. The sample and hold stage acquires the capacitor voltage at its final amplitude and stores the amplitude of this signal in a "holding" memory capacitor. The sample and hold circuit commences its holding operation before the 100 microsecond switch opening period is completed and continues to hold the amplitude for further processing after the capacitor shorting switch has closed. The output signal of the sample and hold stage that results from a sample taken when the lamp was flashed is fed to a high gain (x500) amplifier and then presented to the add/subtract integrator where a fixed time duration sample of the signal voltage is taken and stored as a charge in the "long duration" memory capacitor of the add/subtract integrator. Before the next lamp flash occurs, a control circuit initiates signals that erases the signal stored in the sample and hold memory and starts a new sampling period by sampling the output from the photomultiplier for a 100 microsecond period. But, this time the flashlamp does not flash, so, no fluorescence signal

component is present in the processed signal at the output of the high gain amplifier. The control circuitry routes this signal through a unity gain polarity inverter and then presents it to the input of the add/subtract integrator. Again a fixed time duration sample of the amplitude is taken and added to the memory. The result is that the sample taken when the lamp did not flash is subtracted from the sample taken when the lamp did flash by the add/subtract integrator. This add/subtract routine is repeated for each flash of the measurement cycle, i.e., about 1000 times. The partial sums from the add/subtract routines accumulate to a final value at the end of the measurement cycle. What is accomplished by this signal processing operation is explained below.

The sample that appears at the output of the high gain amplifier stage, corresponding to when the lamp did flash, includes the NO_2 fluorescence signal, the photomultiplier tube dark noise, the dc offset noise introduced by the electronic circuitry and a noise component that arises when the light from the flashlamp shines through the air examination chamber while a NO_2-free gas is present. The sample that appears at the output of the high gain amplifier when the lamp does not flash includes only the photomultiplier dark noise and the electronic circuitry dc offset noise. So, by inverting the polarity of the sample taken with the lamp off and adding it to the sample taken with the lamp on we expected to cancel the electronic circuitry offset noise and the photomultiplier dark noise. The electronic circuitry noise cancelled as expected. However, the dark noise of the uncooled 9659 QAM photomultiplier is of a statistical character and complete cancellation is not expected. Statistical fluctuations in the output of the PMT resulted in an NO_2 detectivity of $\sim$11 ppb. With the photomultiplier tube cooled to $\sim -12^{\circ}C$ the photomultiplier dark noise was reduced and detectivity was improved to $\sim$ 5 ppb.

At the output of the add/subtract integrator there is, in addition to the fluorescence signal component, the noise component that arises when the flash lamp light illuminates a NO_2-free gas, i.e., the air with "zero" NO_2 present. It was expected and experimentally verified that this noise would be essentially a constant value when the lamp energy was held constant during a measurement cycle. A "background suppression" bias control was incorporated to supply a selectable, fixed voltage of opposite polarity to cancel

this noise. The processed signal with the background correction is essentially all due to fluorescence from the NO_2 so the instrument can be calibrated for NO_2 response by measuring the voltage produced at the end of a measurement cycle when a known concentration of NO_2 is present in the air or carrier gas drawn through the chamber during a measurement cycle. It was convenient for us to scale the NO_2 calibration voltage with a ten-turn linear potentiometer by setting the potentiometer dial to a fractional part of the full scale value that equated 1 ppb NO_2 concentration with 1 millivolt of signal. The scaled voltage was presented to the digital voltmeter. The voltmeter reading printed at the end of a reading cycle was in units of millivolts, hence directly equivalent to ppb of NO_2 concentration in the air being examined. Each time a measurement cycle was started the electronic control circuitry erased the accumulated sum in the add/subtract integrator before proceeding with the new measurement. Typically, a calibration measurement yielded 3 millivolts per part per billion NO_2 concentration before scaling by the potentiometer. Considering that this resulted from about 1000 flashes of the lamp it is seen that a single flash of the lamp produced only about 3 microvolts per part per billion NO_2 concentration. Actually, the signal at the output of the photomultiplier tube was a nominal 30 microvolts per flash per ppb NO_2 concentration, but the combined gain of the high gain amplifier and the add/subtract integrator in the PNFM was chosen to be 0.1 from other considerations.

Integration of the fluorescence signal resulting from more than one flash of the lamp is desirable mainly because the gain of the photomultiplier tube is statistical in nature. The averaging technique described above is useful in reducing the statistical fluctuation effect in the measurement signals. Also, the higher voltage amplitudes resulting from the summation of many fluorescence signal samples is more compatible with the electronics of the display system.

The photodiode and optical energy meter controller were identical to those employed in the prototype laser NO_2 monitor developed for EPA under contract No. 68-02-1255. The add/subtract integrator used another of those type units that was modified to perform the integration of electronic signals. The operation controller was constructed using standard TTL logic modules. This unit was designed to facilitate laboratory investigation of several operating regimes of the PNFM.

SECTION 4

CALIBRATION AND LINEARITY TESTS

Calibration and operation of the system was performed in the excitation light control mode in which a readout is obtained after a preset energy has been delivered to the sample from the flashlamp. The controller was adjusted to sense 80 mJ of energy which corresponded to approximately 1000 pulses of the flashlamp. This means that a single measurement of the NO_2 concentration requires about 77 seconds.

As stated earlier, a background offset was incorporated into the system to zero out the background. In addition, the output may be scaled so that the system will readout directly the NO_2 concentration in ppb. In light of this, the system was calibrated and adjusted in the following manner.

First, with pure nitrogen flowing through the chamber, 54 measurements of the background signal were obtained. The average value of the background signal was 508 $\pm$ 11 mV which corresponds to 156 $\pm$ 3 ppb (based on calibration constant determination to be discussed next).

The background offset control was then adjusted to zero out the background. After the adjustment was made, 25 readings were taken of the zero level. The average zero level was -1 $\pm$ 9 mV.

Next a known sample of NO_2 was delivered to the chamber using a standard 1 cm NO_2 permeation tube. Based on the manufacturer's permeation rate data, flow rate, pressure and temperature, the sample NO_2 concentration was determined to be 133 $\pm$ 10 ppb. To provide some information on the measurements involved in the determination of the calibration constant we list the following values: temperature, 24.61 $\pm$ .02°C: pressure, 758 $\pm$ 3 Torr; flow rate, 4.34 $\pm$ 0.17 ℓ/min; permeation rate, 1083 $\pm$ 72 ng/min; NO_2 concentration, 133 $\pm$ 10 ppb. Twenty-five readings were taken of the NO_2 sample. The average value obtained was 433 $\pm$ 4 mV. With a zero level of -1 $\pm$ 9 mV, the NO_2 measurement would be 434 $\pm$ 10 mV, giving a calibration constant of 3.26 $\pm$

.26 mV/ppb or an accuracy of 8%. The system is then scaled for a 1.00 ± 0.08 mV/ppb readout, which provides a direct readout of the NO_2 concentration. Scaling the system, by a factor of 3.26 also scales down the background fluctuations by a factor of 3.26. This means with a 1.00 mV/ppb scale factor and a zero level of 0 ± 4 mV, the minimum detectable level of NO_2 is $(\sqrt{2})$ (4)/1 or 5.7 ppb .

Table 1 lists the calibrations performed on 5 consecutive working days. The purpose of these tests was to demonstrate the repeatability and realiability of the PNFM. The last two entries were made on the two days of ambient air monitoring. Several important facts should be noted from the table: (1) The 3% variation in the scale factor is well within the original 8% uncertainty in determination of the 1.00 mV/ppb scale factor and is mostly due to the 7.5% uncertainty in the NO_2 sample and 6% statistical fluctuation in the NO_2 reading. (2) The apparent change in the zero level is within the statistical fluctuation about the zero level of ± 4 ppb and well within the original uncertainty of the zero setting. (3) The accuracy at the 100 ppb level is ± 8 ppb. (4) Finally, the average minimum level of detectability is 5.6 ± 1 ppb based on the average fluctuations of the zero level of ± 4 ppb and the average scale factor of 0.991 detectability = $\sqrt{2}\,\frac{\text{Zero Level Fluctuation}}{\text{Scale Factor}}$.

One of the most important parameters of the PNFM is that of linearity of response. This has been checked over the range of 30 to 200 ppb and the results are shown in Figure 6. The curve is linear within experimental error. It should be noted that the vertical error bars reflecting the statistical uncertainty of the NO_2 monitor reading are on the order of 10 ppb near zero. This is due to the fact that the data was taken prior to cooling the photomultiplier at which time the detectability had been only 11 ppb. This means knowledge of the zero was certain only to within 9 ppb and could account for the fact that the line does not pass through zero and that all readings are slightly high.

TABLE 1

INSTRUMENT SENSITIVITY

CONSECUTIVE DAILY CALIBRATIONS

Day in March '76	Calibration Number	Zero Level (ppb)	Sample NO_2 Concentration (ppb)	Instrument NO_2 Reading (ppb)	Instrument NO_2 Concentration Including Zero Shift (ppb)	Scale Factor (mV/ppb)	Detectability (ppb)
8	1	-1 ± 4	136 ± 10	133 ± 5	134 ± 6	0.985	5.7
9	2	-1 ± 4	136 ± 10	140 ± 6	141 ± 7	1.037	5.5
9	3	-1 ± 4	139 ± 10	140 ± 6	141 ± 7	1.014	5.6
9	4	-4 ± 4	138 ± 10	134 ± 7	138 ± 8	1.000	5.6
10	5	0 ± 5	136 ± 10	133 ± 6	133 ± 8	0.978	7.2
10	6	-4 ± 3	138 ± 10	138 ± 6	142 ± 6	1.029	4.1
10	7	0 ± 4	136 ± 10	131 ± 8	131 ± 9	0.963	5.9
10	8	0 ± 4	139 ± 10	137 ± 7	137 ± 8	0.986	5.7
17	9	+2 ± 4	123 ± 10	123 ± 8	121 ± 9	0.984	5.7
18	10	0 ± 3	129 ± 10	121 ± 8	121 ± 8	0.938	4.5

INSTRUMENT CAPABILITY = 5.6 ± 1 ppb

SECTION 5

AMBIENT AIR NO_2 LEVELS AT LOCATION OF THE AEROSPACE CORPORATION

After completion of the calibration and linearity tests, the PNFM was used to monitor the ambient air in the vicinity of our building. The general geographical location is just southeast of Los Angeles International Airport near the intersection of Aviation and El Segundo Boulevards. The air sample was drawn into the lab through PVC tubing with an orifice 15 ft above the roof of our building; the overall length of the piping to our chamber was approximately 40 ft. A flow rate of 4.34 liters/min. was used and the air sample was filtered to remove aerosols. Continuous monitoring was performed for 10 hours a day on both the 17th and 18th of March, 1976, with readouts obtained every 2 minutes. The recorded data is shown by the graphs in Figures 7 and 8. The calibration data is also shown for each day. The background fluctuations are only 4 ppb and the undertainty at the sample NO_2 level is about 8 ppb. This is indicated by the error bars on the baseline and 100 ppb level respectively.

On the 17th of March, monitoring began at 7.00 AM with overcast skies and light fog. The relative humidity and temperature was 92% and 60° F respectively. The average NO_2 concentration at this time was only 20 ppb. By 10:30 AM, the temperature had risen to 70° F, the relative humidity had dropped to 38% and the NO_2 concentration had peaked at an average value of 70 ppb. Throughout the day, there was considerable haze with an average temperature and relative humidity of 70° F and 40% respectively. Wind was blowing from the southwest at about 10 MPH. A noteworthy feature is the low level of NO_2 in the afternoon except for the singular strong peak (150 ppb) at 2:15 PM occurring over a half hour interval. The presence of this peak is not fully understood. On the 18th of March, monitoring began at 7:30 AM with heavy fog. The relative humidity was again 92% with a temperature of 56° F. But in contrast to yesterday at this time the average NO_2 concentration was

55 ppb. By 10:00 AM, the temperature had risen to 60° F, the relative humidity had dropped to 50%, and the NO_2 concentration had again peaked at about 75 ppb. Light haze existed throughout the morning but by 2:00 PM the haze had disappeared with clear skies and extremely good visibility. Wind was still from the south-west with gusts up to 18 MPH. During the afternoon the lowest levels of NO_2 concentration, from 5 to 10 ppb, were observed. At 5:00 PM a second peak of about 35 ppb was observed which may be correlated with the onset of automobile traffic.

A feature of our measurement technique was the ability to monitor rapid variations in concentration. Much detail of this type is clearly exhibited by the data in Figures 7 and 8.

SECTION 6

SUGGESTIONS FOR IMPROVEMENTS IN PERFORMANCE OF THE PNFM

It is almost axiomatic that improvements in the PNFM will be required as the range of application expands. These design modifications will encompass virtually all aspects of the instrument. In particular, designs leading to greater compactness and mechanical conveniences are desirable. It is almost superfluous to state that increased sensitivity will be required.

Tests have shown that the length of the input arm which contains the flashlamp (Fig. 2) can be substantially reduced. It is obvious that other dimensions can also be reduced. We estimate that the longest dimension of a fully packaged unit should be less than 75 cm.

The electronic circuitry developed for the PNFM can certainly be minaturized and redesigned for even higher performance. Nevertheless, the electronics package is probably furthest along in refinement as compared to the mechanical and optical design of the unit.

Increased sensitivity can be obtained by incorporation of the following suggested design modifications (1) lamp output - the flash lamp is currently used at 1/3 its output rating. By increasing the light output per flash, greater sensitivity can be obtained. A well designed reflector, placed in back of the flashlamp to redirect this light along the input arm of the tube might almost double the useful light output of the lamp. (2) reduced background - it appears that the potential for radical improvement in sensitivity is in the direction of reduction of background. Considerable effort was expended along these lines but much remains to be done, such as improved collimation of the pump light and improved coatings for the fluorescence chamber (coatings that absorb the scattered blue light with an absolute minimum of red fluorescence).

The statistical fluctuations of the PMT dark current from an uncooled

PMT presently limits the detectability to about 11 ppb. Cooling the PMT eliminates the dark current and increases the detectability; an alternative to cooling is to redesign the electronics to accept dark current pulses for a shorter length of time. At present, the electronic control packages record PMT currents for a duration of 100 us for each flashlamp light pulse which is approximately 7 us in duration. A reduction in this gate width could lead to a reduction in PMT dark current and other noise signals without adversely reducing the fluorescence signals. Optimizing the duration of this gate and its position with respect to the flash lamp pulse should improve the sensitivity of the unit.

It appears to us, that a four-fold improvement in sensitivity should be readily achievable. Thus we can look forward to an improved instrument, more compact than the present phototype with a sensitivity of about 1 ppb.

REFERENCES

1. M. Birnbaum and A. W. Tucker, "NO_2 Measuring System", Final Report on Contract No. 68-02-1255, EPA-650/2-74-059, 31 pp., May 1974.

2. J. A. Gelbwachs, M. Birnbaum, A. W. Tucker and C. L. Fincher, "Fluorescence Determination of Atmospheric NO_2", Opto Electronics, 4: 155-160, 1972.

3. A. W. Tucker, A. Petersen and M. Birnbaum, "Fluorescence Determination of Atmospheric NO and NO_2", Appl. Optics, 12(9): 2036-2038, 1973.

4. A. W. Tucker, M. Birnbaum and C. L. Fincher, "Atmospheric NO_2 Determination by 442 nm Laser Induced Fluorescence", Applied Optics, 14(6): 1418-1422, 1975.

5. M. Birnbaum, "Laser-Excited Fluorescence Techniques in Air Pollution Monitoring", Modern Fluorescence Spectroscopy; Vol. 1, edited by E. L. Wehry. Plenum Publishing Corp., New York, 1976, pp. 121-157.

6. A. M. Winer, J. W. Peters, J. P. Smith and J. N. Pitts, Jr., "Response of Commercial Chemiluminescent NO - NO_2 Analyzers to Other Nitrogen-Containing Compounds", Environ. Science and Technology, Vol. 8, pp. 1118-1121, 13 December 1974.

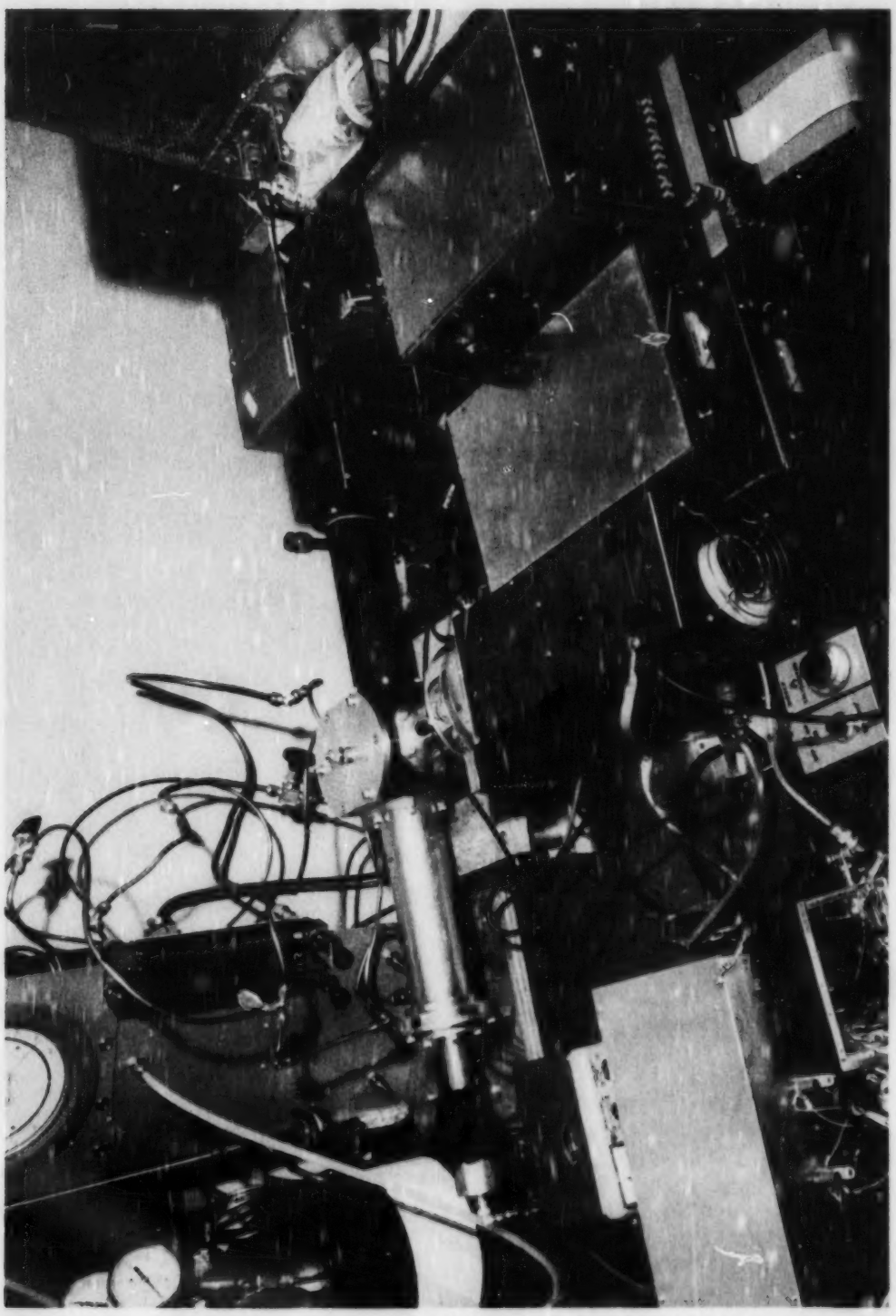

Figure 1. Pulsed NO_2 Fluorescence Monitor.

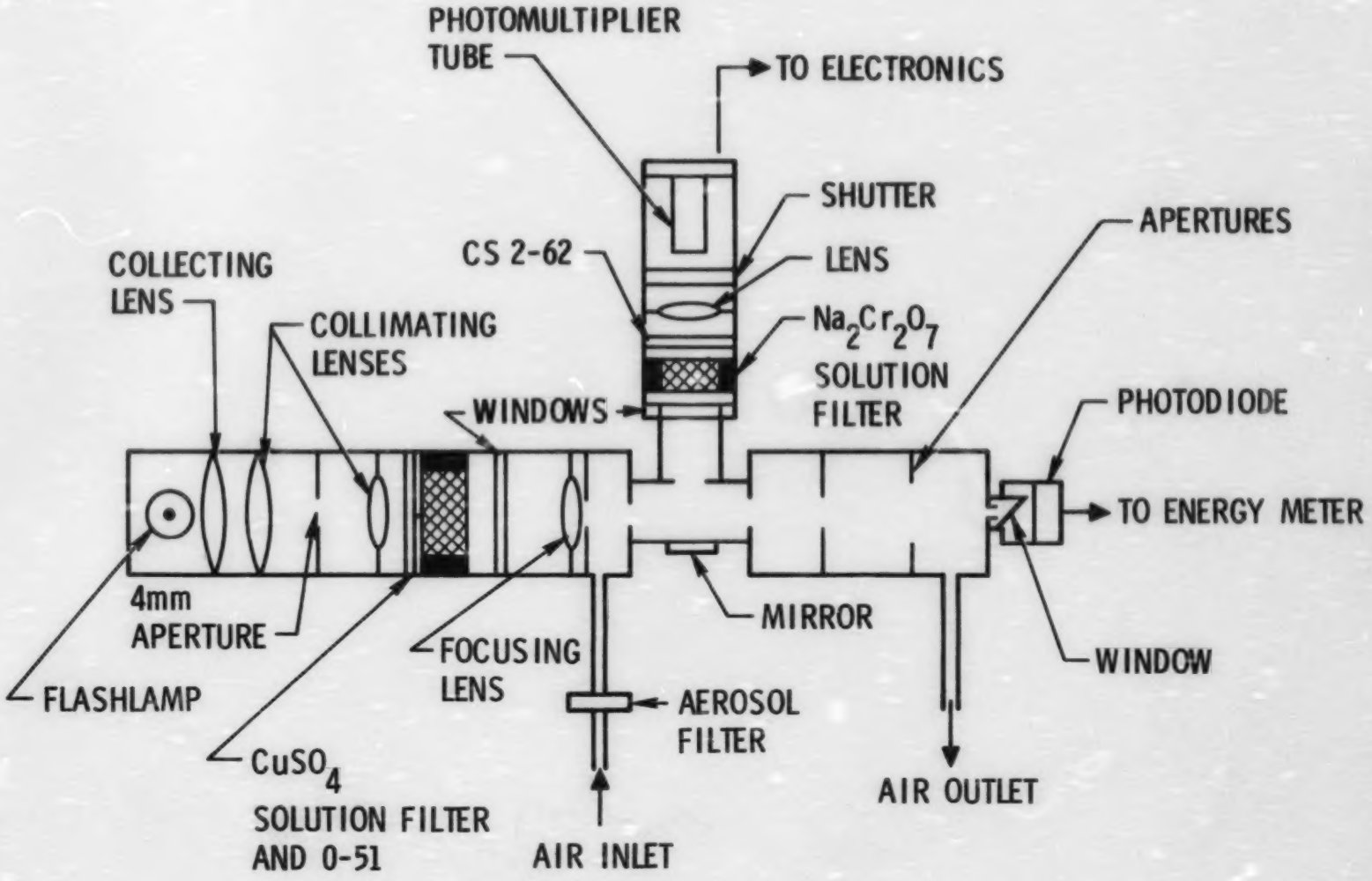

Figure 2. Block Diagram of Optical Subsystem.

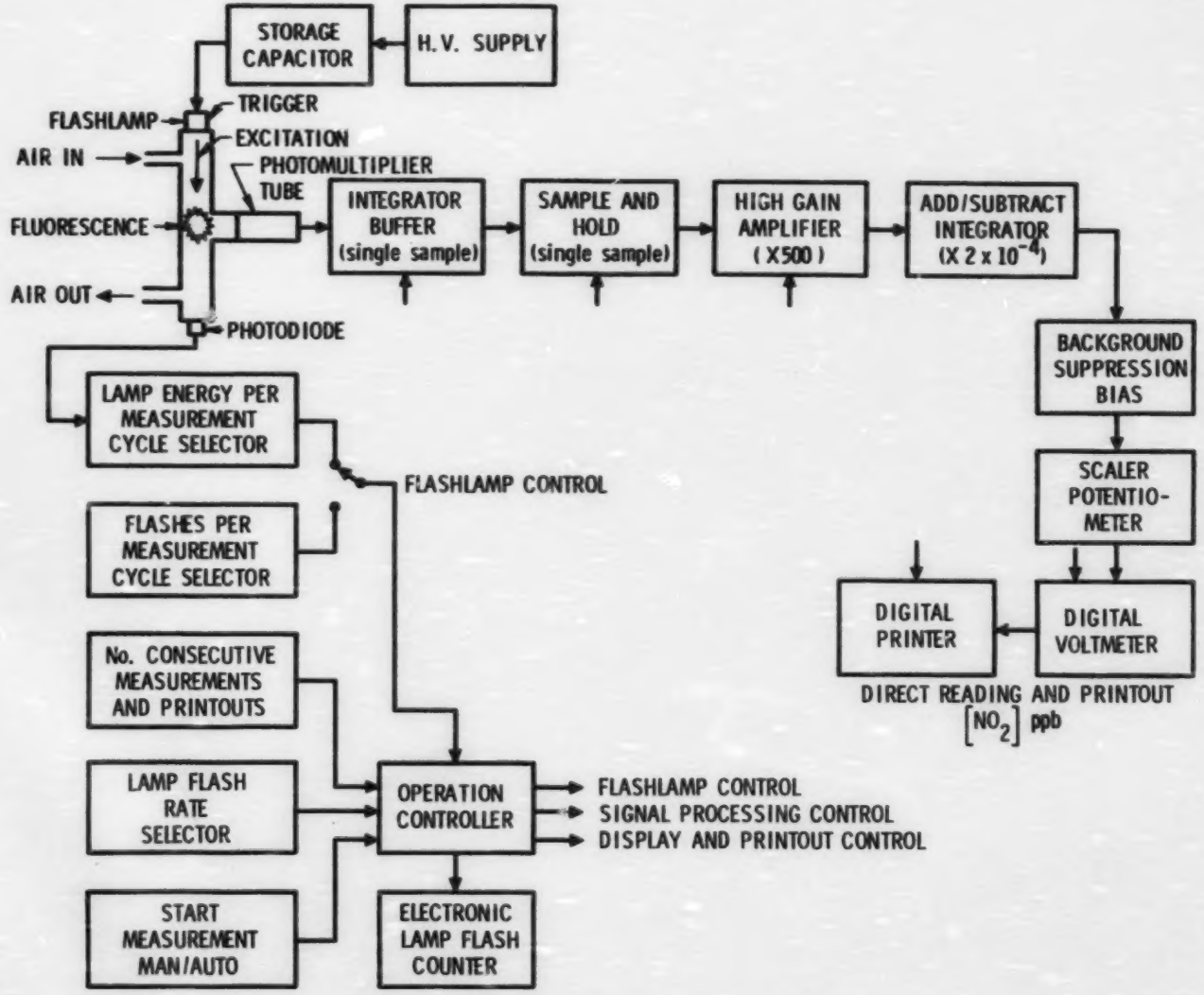

Figure 3. Block Diagram of Electronic Subsystem.

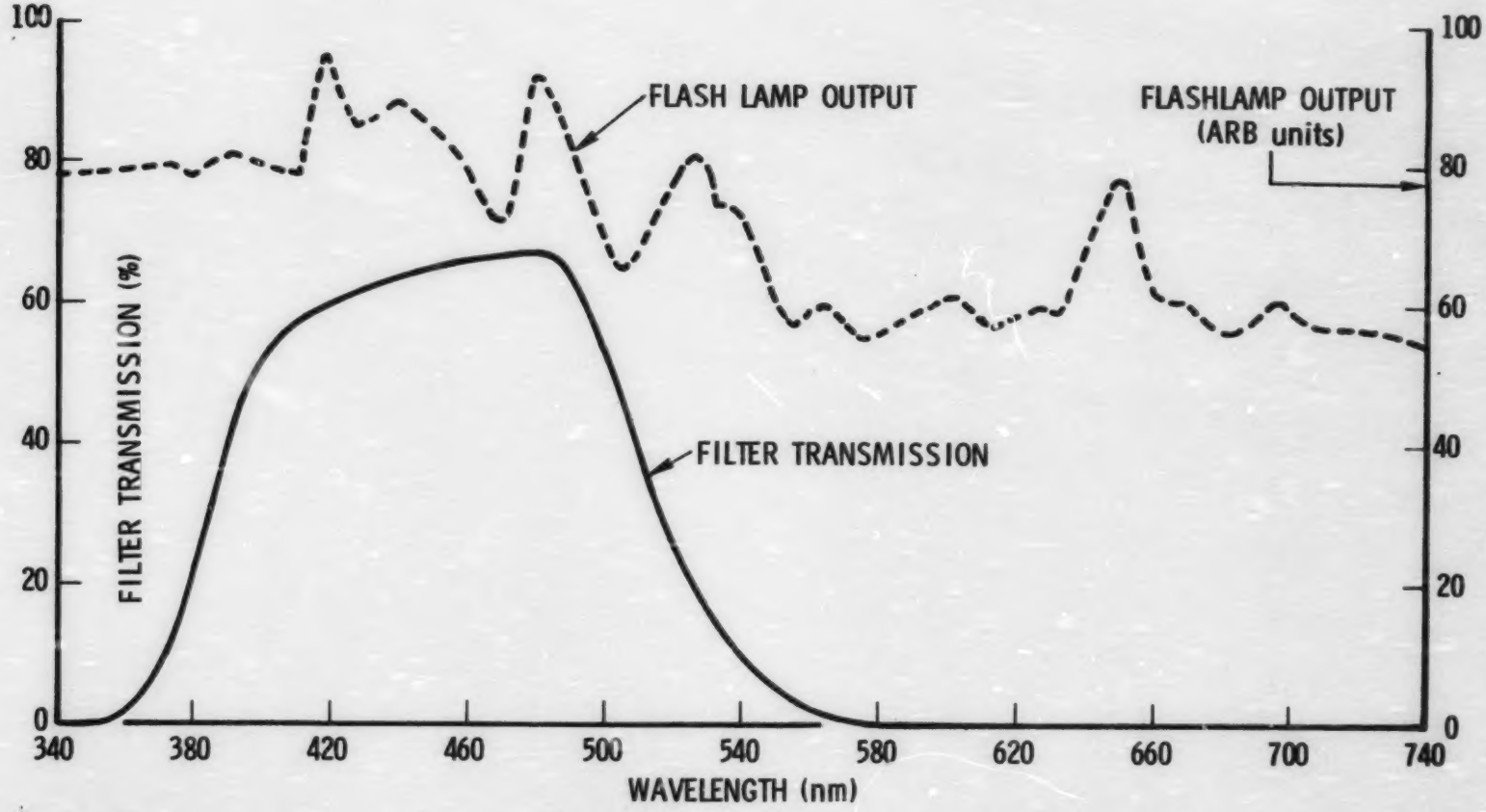

Figure 4. Spectral Transmission of the Flashlamp Filter (5 cm Path of 300 grams per liter $CuSO_4$ Solution plus Corning Glass CS 0-51 Filter). Spectral Output of Xe Flashlamp. (Dashed Line)

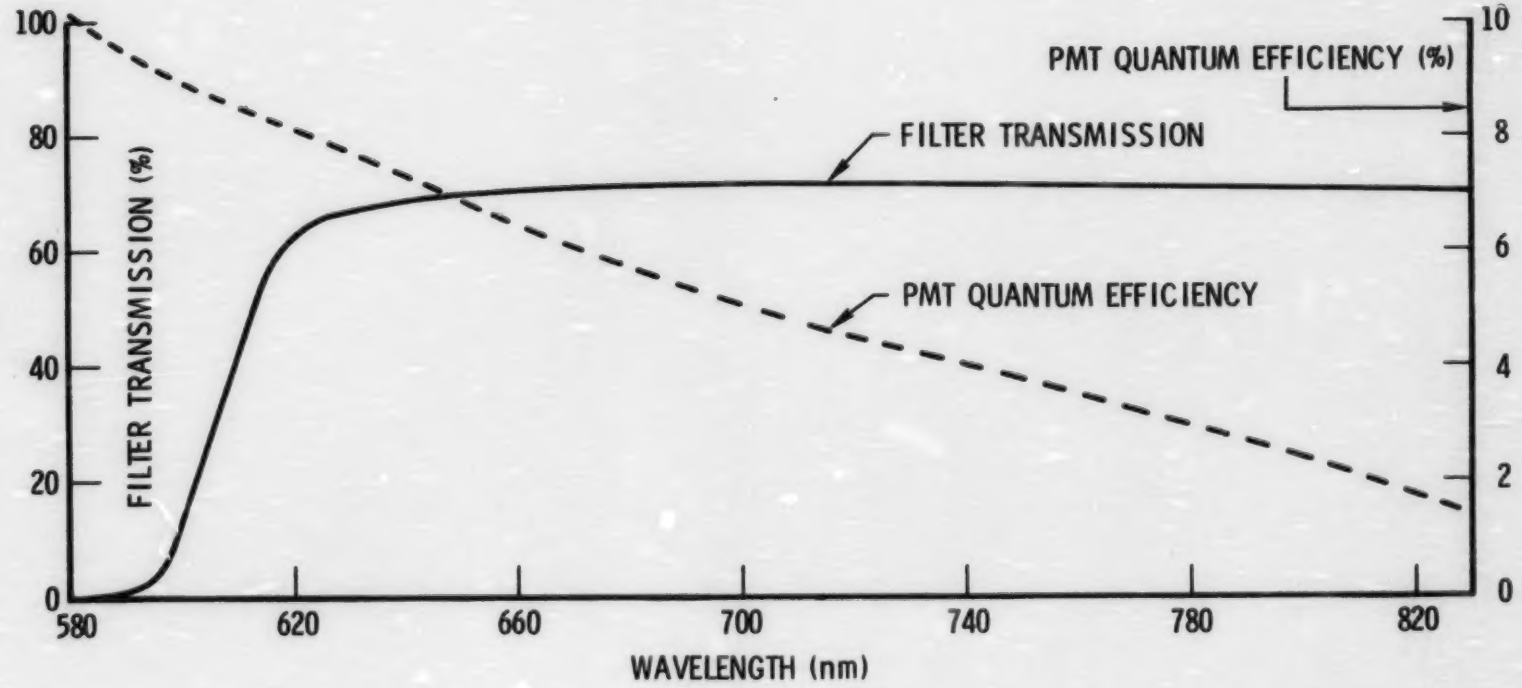

Figure 5. Spectral Transmission of the PMT Filter (2 cm Path of 304 grams per liter $Na_2Cr_2O_7$. $2H_2O$ Solution Plus Corning Glass CS 2-62 Filter). Spectral Response of EMI 9659 QAM PMT (Dashed Line).

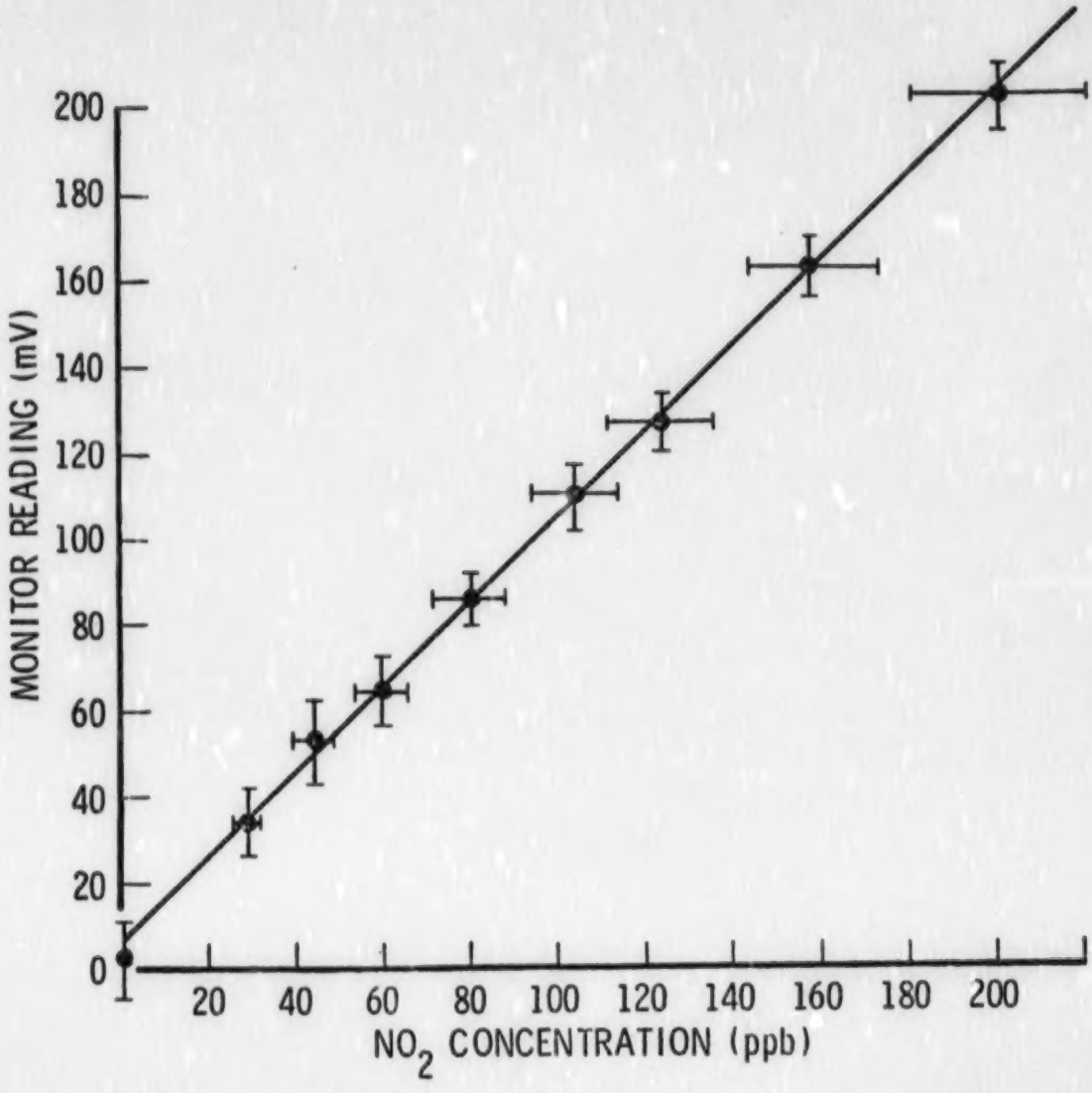

Figure 6. Linearity Test for NO_2 Monitor in the 30 to 200 ppb Range of NO_2 in Nitrogen

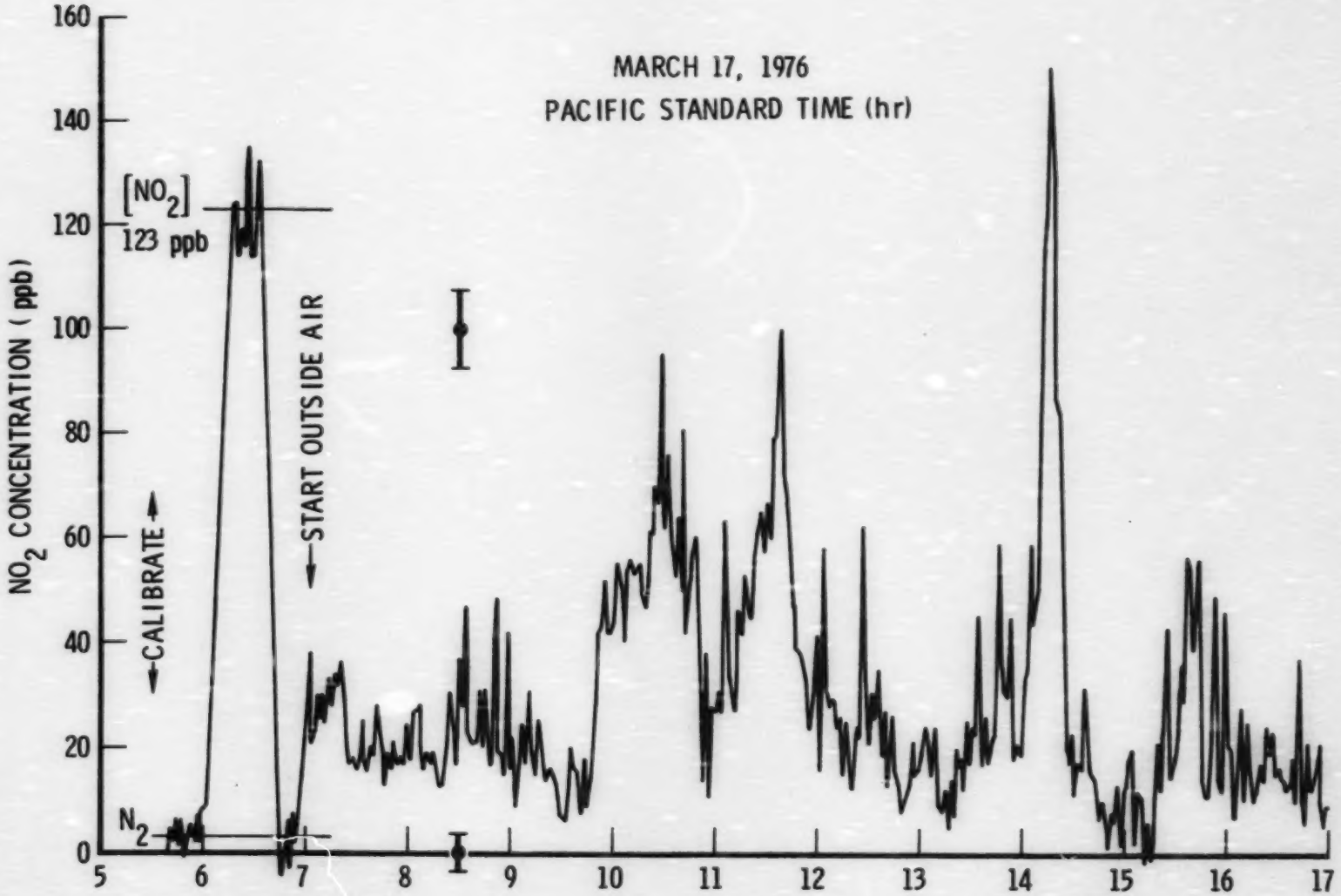

Figure 7. Atmospheric NO_2 Concentrations, El Segundo, California, March 17, 1976

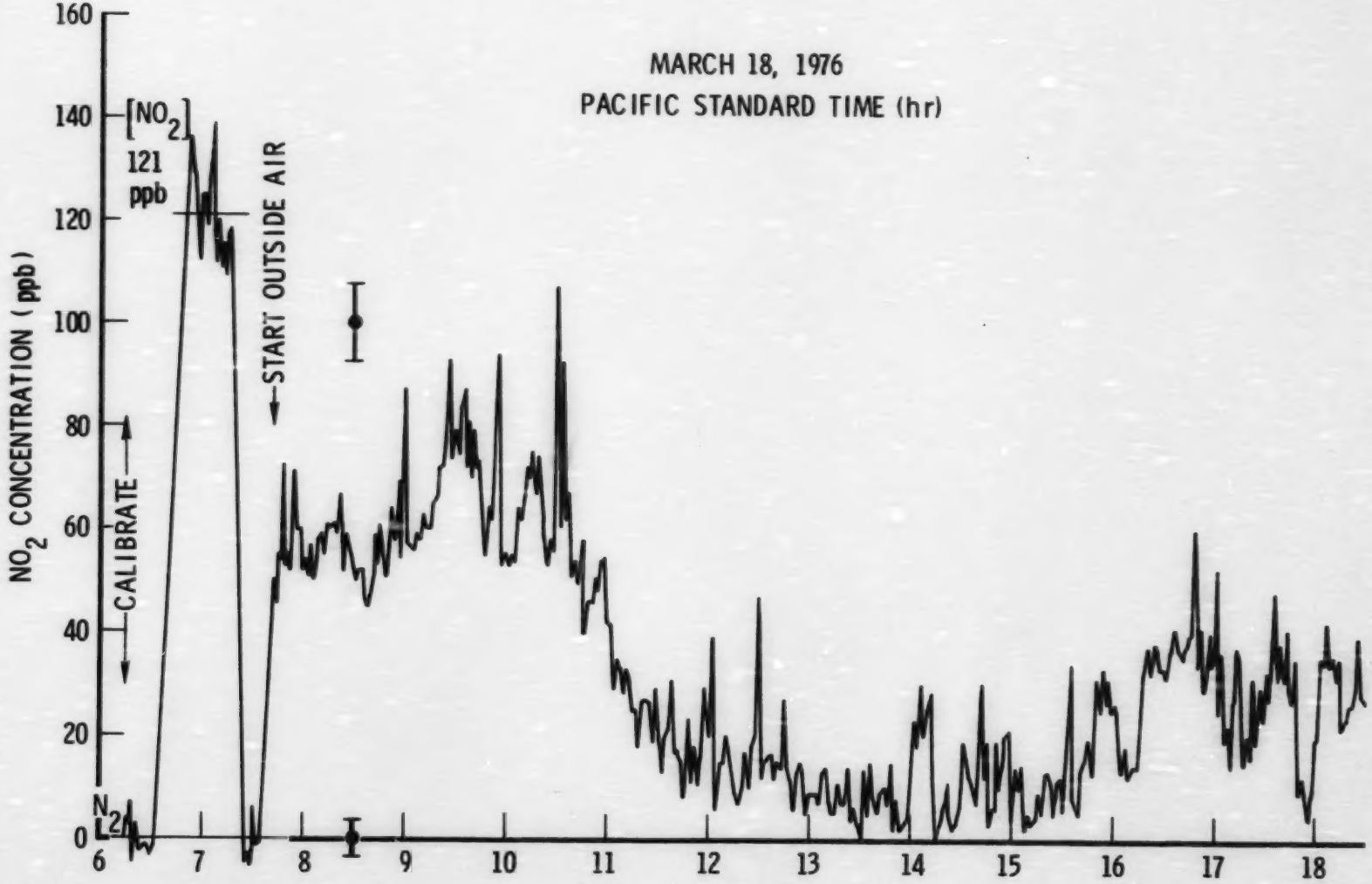

Figure 8. Atmospheric NO_2 Concentrations, El Segundo, California, March 18, 1976.